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Paper No. 18

BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

Application Number: 09/832,141
Filing Date: April 09, 2001
Appellant(s): CHRISMAN, JOHN W.

Bradley Jensen
For Appellant

EXAMINER'S ANSWER

This is in response to the appeal brief filed 1/3/03.

(1) Real Party in Interest

A statement identifying the real party in interest is contained in the brief.

(2) Related Appeals and Interferences

A statement identifying the related appeals and interferences which will directly affect or be directly affected by or have a bearing on the decision in the pending appeal is contained in the brief.

(3) Status of Claims

The statement of the status of the claims contained in the brief is correct.

(4) Status of Amendments After Final

The appellant's statement of the status of amendments after final rejection contained in the brief is correct.

(5) Summary of Invention

The summary of invention contained in the brief is correct.

(6) Issues

The appellant's statement of the issues in the brief is correct.

(7) Grouping of Claims

Appellant's brief includes a statement that claims 1,10, 20 and 27 do not stand or fall together and provides reasons as set forth in 37 CFR 1.192(c)(7) and (c)(8).

(8) Claims Appealed

The copy of the appealed claims contained in the Appendix to the brief is correct.

(9) Prior Art of Record

4,722,815	Shibanai	2/1988
4,293,602	Coffey et al.	10/1981
4,762,493	Anderson	8/1988

(10) Grounds of Rejection

The following ground(s) of rejection are applicable to the appealed claims:

Claims 1-3, 5, 7, 8, 10-27, 29 and 31 are rejected under 35 U.S.C. 103(a) as being unpatentable over what is old and well known in bowling balls in view of Shibanai.

As to claims 1-3, 5, 7, 10-19, 20-27, 29 and 31, bowling balls of nonporous polymeric thermosetting resin is old and well known. This is admitted old at the bottom of pg. 2 of Appellant's specification. Lacking in bowling balls is the use of a fragrance. However, perfumed polymers intended for the purpose of making plastic articles with a fragrance are also well known. Shibanai teaches compounds to be included in synthetic resin products in order to enhance their smell. While there is no direct teaching of using his compound in a bowling ball, it has been held that, in evaluating a reference, it is proper to take into account not only the specific teaching of the reference(s) but also the inferences which one skilled in the art would reasonably be expected to draw therefrom. In re Preda, 401 F.2d 825, 826, 159 USPQ 342, 344 (CCPA 1968). Additionally, one must observe that an artisan must be presumed to know something about the art apart from what the references disclose (see In re Jacoby, 309 F.2d, 513, 516, 135 USPQ 317, 319 (CCPA 1962). In line with this, one skilled in the art would clearly have found it obvious to have applied perfumed compounds, such as Shibanai's in order to make a bowling ball smell better. Where the claims call

for a two-part resin and the fragrance being dissolved therein, Shibanai directly teaches that "it is also possible to mix perfume...with a synthetic resin compound followed by molding" (col. 1, ln. 26) but that this "direct addition of perfume...to synthetic resin compound is not as effective as it seems" (col. 1, 35). Hence Shibanai goes on to teach an improved more effective method of adding fragrance to a product that includes forming an inclusion compound consisting of perfume included in cyclodextrin. While Shibanai does not detail the old and known methods of "mixing perfume" and "direct addition of perfume" that is at least partially dissolved within the resin, such are considered old when one further considers Coffey et al. as an example. Coffey teaches that it is an old expedient and would have been obvious to mix fragrances to two part resins in the forming of a fragrances polymer product. Edwards and Wilbert, are further examples of direct mixing of fragrances with a polyurethane prior to molding. The art is replete with the successful addition of fragrance to two part polymer products. The motivation is simply to "impart to other polymeric products pleasant odors" (Wilbert, col.1, ln. 57).

The amount of fragrance as called for in claim 8 is considered and obvious matter of choice depending upon how strong of a smell is desired.

Claims 9, 32 and 33 are rejected under 35 U.S.C. 103(a) as being unpatentable over bowling balls in view of Shibanai and further in view of Anderson.

Applying a pigment to polymer resin products to give them color is old and well known. Anderson teaches that it is old to apply a color that correlates to a fragrance in a product. To have done so with a bowling ball would have been obvious to one skilled in the art for the novelty.

Applicant's arguments with respect to claims 1-33 have been considered but are moot in view of the new ground(s) of rejection.

(11) Response to Argument

SECTION A and B

Appellants remarks are noted but no response is deemed necessary since they merely set forth his interpretation of controlling case law and the applied art.

SECTION C

In the first office action, the applied art and the rejection set forth by the examiner made it clear that adding fragrance in general to plastics is old and well known. Shinbanai, the primary reference, shows a plastics additive

containing perfumes and gives numerous examples pertaining to its use in thermoplastics. In response to this first office action, appellant added the term "two-part resin" to the claims.

First, one must look at the terms used in the claims in order to determine their scope. As such it is necessary to review the specification order to establish whether the meaning of those terms and phrases given by the applicant in the context of the application should be accorded any meaning different from the usual and customary meaning of the claim terms. Upon doing such, it can be concluded that any plastic made up of two components can be considered a "two-part resin". Supporting this conclusion can be found in the specification where it notes that "conventionally, bowling balls have been formed from machinable, thermosetting plastic materials." (pg. 2, [0002]). Paragraph [0004] of pg. 2 discusses reactive polymers that require the addition of a catalyst for polymerization. Nowhere in the specification does appellant consider or define polymers requiring a catalyst (such as the ones discussed in paragraph [0004]) to be defined as "two-part resins". Compounded by the fact that many known thermosetting resins contain other numerous components such as fillers, promoters, inhibitors and reactive components such as isocyanates (used commonly to produce polyurethane foams or cellular rubber). To the extent that known thermosetting resins can be "two-part" based upon its composition including more than one component in its making, there is no distinction between the "thermosetting" resins to which Shibanai discloses adding his fragrance material and one, such as an epoxy resin, requiring a catalyst. For example Shibanai is considered to disclose a "two-part" resin of a "synthetic resin compound and glycitol(s)" (col. 17, ln. 51).

Lastly, even if one were to recognize the term of "two-part resin" to mean a polymer of the type requiring a resin. These resins are still "thermosetting resins" per se. However, the heat required for polymerization is provided by a chemical reaction (. Note pg. 4 of the Handbook of Reinforced Plastics that list "epoxy resins" as a "thermosetting resin". On pg. 71, ln. 16, these epoxy resins are of the type requiring "hardeners or curing agent" that react to polymerize the resins. As can be clearly seen by the Handbook, one skilled in the art of plastics fully recognizes the uses, properties and manufacturing practices for making products and selecting a material for its intended purpose.

Appellant's initial remarks at the top of pg. 11 of the Brief alleging that Shinbanal are "limited to use of a thermoplastic resin" are moot in view of the ordinary level of skill as discussed above. In the first point above, it is shown that thermosetting resins, such as those in Shinbanal, can be considered to be "two-part" resins within the scope of the claims since they can contain fillers and other additives. In the last portion of the discussion above, it is shown that there is no distinction in the art between "one-part" and "two-part" resins as implied by appellant. Even

though a polymer requires a catalyst for polymerization (as opposed to external heat) as in the case of an epoxy resin, such are still considered to be "thermosetting resins".

Claims 11-13, 18 and 19, including polyol in the method of manufacturing of a bowling ball is old. This is admitted by appellant on his specification, paragraph [0004]. To further assist the Board in making its determination and to appropriately determine what is known in the art, the examiner has appended two websites that discuss the uses of Polyol with respect to polyurethanes. Note http://www.kosa.com/poly/specprod.htm and http://polyol.synair.com/About%20Polyols.htm, copies of which are appended to this examiners answer.

As to claim 20, skill has to be presumed on the part of a person practicing the invention of Shinbanai. Known is that once the catalyst is added to polyol, there a "working time" for the resin is set. Mixing the fragrance into the polyol prior to the catalyst does nothing more than what would be obvious to the skilled artisan. Further, it is clear that the fragrance could be added to the polyol after the addition of the catalyst. However, it would need to be done such that it could be uniformly mixed and molded before polymerization were to begin.

As to claims 20 and 21-26, the removal of gas "trapped" in a polymer mixture is old and inherent in the art of plastics. Failure to do so results in an inferior final product made by the visibility of "bubbles" that art trapped after the product has fully cured. Surely applicant is not the inventor of removing trapped air or gas known throughout the plastics industry.

As to claim 21, Webster's New World Dictionary defines "dissolve" as "to merge with a liquid". Shinbanai clearly teaches a fragrance that is to be "merged" with a liquid polymer. As such, claim 21 is considered fairly taught.

As set forth above, a catalyst is well known as being used with polyols to cause polymerization. The use of a catalyst as called for in claim 23 is not new to the art of plastics.\

The use of isocyantes as called for by claim24 is old. The Boards attention is drawn to pg. 5 of the Handbook. As mentioned previously in the Answer, they are mostly known for having a "foaming" affect on plastic compositions.

Claims 27, 29 and 31 amount to a mere allegation of patentability base on their dependency of claim 1. Since claim 1 has been shown above not to be patentable, these claims too are considered not patentable. Neither Shinbanai nor Coffey "teach away" from the instant invention as appellant states at the top of pg. 13. Well known is that the teaching of Shinbanai and Coffey are to be read in light of what is known in the prior art and for what they "would suggest". As noted by Shinbanai, the direct addition of certain addatives (for example insecticides) are "so volatile, liable to denature and unstable to heat that it is difficult to practice to mold a mixture" (col. 1, ln. 40). He suggest the it is clearly possible. However, Shinbanai's invention makes it easier and is an improvement upon

traditional methods of directly adding such substances to a synthetic resin product. Further note that an artisan is not compelled to blindly follow the teaching of one prior art reference over another without the exercise of independent judgement. *Lear Siegler, Inc. v. Aeroquip Corp., 733 F.2d 881, 889, 221 USPQ 1025, 1032 (Fed. Cir. 1984).* First, one skilled in the art would not consider the teachings of Shinbanai to be restricted to thermoplastics or thermoset resins. Second, as stated above and as taught by Handbook, two-part resins such as "epoxy" are known to be classified as a thermoplastic.

One wishing to enhance the "smell" of a bowling ball would clearly consider what others before them have done to make other plastic product smell better. As such both Shinbanai and Coffey are directly analogous to the problem at hand.

The discussion of "hook" has little to do with whether or not one would be motivated to add fragrance to a plastic product. True bowling ball designers a greatly concerned with the surface properties of a ball that affects its performance. However, there are no suggestions that the addition of an inert substance or filler would change the performance of the ball. Nor is there any evidence of record that appellant has overcome any particular performance problems faced with adding fragrances to bowling balls. Lastly, it is to be noted that the design of bowling balls has been mostly a trial and error process. A ball of a particular compound is made and then its performance is noted. How a ball performs and "hooks" depends upon the preference and style of the bowler. The word "motivation" or a word similar to "motivation" does not appear in 35 U.S.C. § 103(a). While a finding of "motivation" supported by substantial evidence probably will support combining teachings of different prior art references to establish a prima facie obviousness case, it is not always necessary. For example, where a claimed apparatus requiring Phillips head screws differs from a prior art apparatus describing the use of flathead screws, it might be hard to find motivation to substitute flathead screws with Phillips head screws to arrive at the claimed invention. However, the prior art would make it more than clear that Phillips head screws and flathead screws are viable alternatives serving the same purpose. Hence, the prior art would "suggest" substitution of flathead screws for Phillips head screws albeit the prior art might not "motivate" use of Phillips head screws in place of flathead screws. What must be established to sustain an obviousness rejection is a legally sufficient rationale as to why the claimed subject matter, as a whole, would have been obvious notwithstanding a difference between claimed subject matter and a reference which is prior art under 35 U.S.C. § 102. Once a difference is found to exist, then the examiner must articulate a legally sufficient rationale in

support of a §103(a) rejection. The legally sufficient rationale may be supported by a reason, suggestion, teaching or motivation in the prior art which would have rendered obvious the claimed subject within the meaning of § 103(a). *In re Dance*, 160 F.3d 1339, 1343, 48 USPQ2d 1635, 1637(Fed. Cir. 1998) (there must be some teaching, suggestion or motivation in the prior art to make the specific combination that was made by the applicant); *In re Gartside*, 203 F.3d 1305, 1319, 53 USPQ2d 1769, 1778(Fed. Cir. 2000) (the best defense against the subtle but powerful attraction of a hindsight-based obviousness analysis is rigorous application of the requirement for a teaching or motivation to combine prior art references); *Pro-Mold and Tool Co. v. Great Lakes Plastics Inc.* 75 F.3d 1568, 1573, 37 USPQ2d 1626, 1629(Fed. Cir. 1996) ("there must be a reason, suggestion, or motivation *** to combine [the teachings of] *** references ****"). Hence, whether bowling balls "hook" or not, does nothing to show insufficient motivation to combine the references where the prior art teaches it is desirable to add fragrance to polymer products.

As to Sinbanai, Coffey and Anderson, Anderson was added to teach the adding color pigments that "match" the "smell". Such a connection between sight and smell is well known in the art. As such to have a red bowling ball that smells of strawberries is not considered a patentable advance as fairly taught by the applied art.

For the above reasons, it is believed that the rejections should be sustained.

Respectfully submitted,

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wp
April 7, 2003

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comparatively low molecular-weight epoxy resin, the epoxide equivalent for which has been determined at 180, the required amine parts per hundred of resin are calculated by:

$$\frac{180}{20.7} = \frac{100}{X}; \quad X = 11.4 \text{ phr.} \qquad (3)$$

This checks closely the empirically determined value of 12 phr for DTA. The theory bearing on these calculations is more completely discussed elsewhere.[28, 29]

Determination of calculated values should serve only as a starting point from which to make empirical evaluation of the required amount of curing agent vs. optimum cast resin or laminate properties. No fully reliable systems other than empirical determination are, according to the best information at hand, available for predicting required amounts for curing agents other than the amines. However, for anhydrides, 0.85 to 1.0 mole of anhydride per epoxy equivalent is regarded as a starting point for empirical phr determination.[28] Mathematical determination of required phr for other than primary or secondary amines may be complicated by side reactivity of some of the groups bearing reactive hydrogen atoms.

In addition to knowing epoxide equivalent for catalyst determination purposes, viscosity, average molecular weight and softening temperature may be used to categorize epoxy resins.[4, 28] Rapid characterisation of curing systems can be made by using the heat-deflection temperature method (ASTM D648).

Glycidyl ether is the product resulting from the reaction of a phenol and a compound containing epoxy groups, usually epichlorhydrin.

Reactive Diluent[28]

A resin manufacturer or formulator will either supply separately or incorporate into epoxy resins diluents or modifiers which will selectively alter properties to suit specific requirements. Reactive diluents are liquid materials added to an uncured epoxy resin primarily to lower viscosity and provide better workability. Reactive diluents are assimilated into the resin network during cure and may not be removed by solvent extraction. Actually any liquid aliphatic or aromatic hydrocarbon that contains an epoxide group and has lower viscosity than the resin may be used as a diluent.

Reactive diluents are of two types. Monofunctional diluents react to terminate chain growth. Polyfunctional diluents become bound more tightly into the resin network because they have more than one reaction site. However, the total amount of either type which may be added to the resin must be limited because degradation of optimum cured properties results with excessive diluent additions.

Examples of monofunctional reactive diluents:
- Butyl glycidyl ether
- Allyl glycidyl ether
- Phenyl glycidyl ether
- Glycidyl methacrylate
- Styrene oxide
- Olefin oxides
- Alicyclic epoxides (limonene monoxide)

Examples of polyfunctional reactive diluents are:
- Butanediol diglycidyl ether (diepoxide)[28]
- Dicyclopentadiene dioxide
- Vinylcyclohexane dioxide
- Epoxidized glycerol
- Difunctional epoxy silicones

Nonreactive Diluents

These comprise materials which do not contain epoxide groups, but which are completely taken up in the cured epoxy resin network. Nonreactive diluents may usually be removed by solvent extraction from the cured resin. Examples are:
- Transphalt (polymeric polynuclear aromatic hydrocarbons)
- Styrene
- Xylene
- Pine oil
- Chlorinated phenyls
- Coal tar

Miscellaneous Modifiers

These are a third type of material useful in changing the workability properties of epoxy resins.[4, 28, 29, 30, 32] In some cases, the epoxy resin may be considered to upgrade the properties of the modifying material, i.e., improving adhesion, heat resistance and mechanical strength. Examples are:
- Polyamides
- Polysulfides
- Triphenyl phosphite
- Furfuryl alcohol
- Asphaltic resins
- Most all thermosetting and some thermoplastic resins

Fillers may be added to epoxy resin batches to reduce shrinkage, lower resin cost and provide other well-known filler advantages (see Sect. III).

ADVANTAGES AND DISADVANTAGES[1, 2, 4, 17, 28]

Considerable additional knowledge of epoxy resins may be gained by considering a full list of advantages and disadvantages, and referring to polyester resins as a criterion.

Advantages

Curing Shrinkage. A volume shrinkage of from 1 to 6% occurs in epoxies compared with 7 to 10% for polyesters. Volume shrinkage has been determined by both dilatometric and density-change methods.[28] The dilatometric method shows higher but more reproducible values. Linear shrinkage is generally determined as being one-third the volumetric shrinkage, and is of prime importance in end applications, principally tooling. Different curing agents have a variable effect on total volumetric shrinkage with most pure curing agents providing straight-line shrinkage vs. time variation (diethylaminopropylamine), and mixed amine compounds (organic salt-tertiary amine mix) showing discontinuity.[28]

It is desirable to develop systems in which gelation occurs as near as possible to the final cure, so that stresses caused by posthardening dimensional changes will be minimised. This is accomplished by plotting curves of volume shrinkage (hence degree of epoxy group conversion) vs. time after catalysing,[4, 28] and recording on the curve the gel point, determined separately by probing a separate sample of the specific resin-hardener mix.[28]

The linear thermal expansion of a 180 epoxide-equivalent resin plus meta-phenylene diamine (14.5 phr) after complete cure of two hours at 302°F was determined to be 0.45×10^{-6}, but was 0.60×10^{-6} after initial cure (149°F).[28]

Cured Properties. The large number of usable curing agents, diluents, and modifiers makes possible a wide variation of cured properties in epoxy-based Reinforced Plastics. The same diversity of basic resin compositions that is required in polyester resins is not necessary with epoxies. Also the curing agent-resin ratio is not as critical as for polyesters.

Odor. There is very little or no odor evolving from a cured epoxy resin.

Dimensional Stability. As pointed out, epoxies possess low thermal expansion, and good chemical[4, 28, 29] and weathering resistance. Heat deflection values are good criteria for chemical resistance under stress.[28] These combined properties make possible epoxy Reinforced Plastics with superior freedom from cracking, crazing and erosion over long periods of in-use exposure.[28]

Creep tendency is lower for epoxies than for polyesters and phenolics, and may be further minimised by postcuring and by exercising or cycling.[28, 29] An example of a low-creep epoxy structure made so by exercising or systematically flexing following postcure is shown in Figure II-3.1.

Adhesion. Probably due to assimilation of hydrogen groups from amine curing agents and to low surface tension, epoxy resins have adhesion superior to that for polyesters and will bond to a wide variety of other substrates.[28]

Electrical Properties. Electrical properties for cured epoxies are superior to those for polyester resins.

High-Temperature Resistance. Whereas the maximum operating level for any polyester resin is 350°F, epoxy compositions may be formulated which will retain a high percentage of original strength at 500°F. Also, epoxy resins have found use in charring and ablative applications.

Dispenser Application. Epoxies have successfully been adapted to industrial liquid dispensing or extruding gun applications due to the convenient mixing ratios of resin and hardeners.

Shelf-life. Storage times for uncatalyzed epoxy resin are generally longer than those for polyesters. Epoxy resins can be B-staged using aromatic amine hardeners.[28] Molecular sieves (porous powders) are used to contain hardener and are mixed into epoxy resins prior to shipment, thus providing a one-component system. The hardener is discharged into the resin when desired by a chemical release agent or by heat. Room-temperature catalysed pot lives of epoxy-hardener mixes vary with resin and hardener types as shown, but may be extended as much as 30% by pouring the batch into a shallow tray after mixing.

Prepregging. Epoxy resins may be readily adapted to prepregging using glass fabrics or roving, and possess catalysed shelf lives of six months or longer when refrigerated.

Figure II-3.1. Helicopter rotor blade fabricated using directed fiber (systematically oriented) epoxy prepreg material. A flexural load (30% of ultimate) sustained for 18 months does not produce permanent deflection after the first 1.5 months following load application. The blade was also designed to withstand over 30,000,000 cycles torsional vibration of ±3200 inch-pounds. (*Courtesy Kaman Aircraft Corporation*)

Air Inhibition. Epoxy resins will normally cure tack-free on air-exposed surfaces except when certain types of amine adduct hardeners are used. No additives are required as for polyesters.

Toughness. Cured epoxy resins possess a high degree of innate cohesive strength and maintain this strength due to the low curing shrinkage.

Metallic Fillers. Powdered metallic fillers such as aluminum, iron, or copper do not react with epoxy resins and hardeners to drastically shorten gel and cure times as they do for polyester resins and promoter-inhibitor-catalyst systems.

Use with Foam Plastics. Fluid epoxy resins, when laid up as a reinforced structure in direct contact with solid foamed styrene plastic, will not dissolve or deform the foam material as will the styrene monomer in polyester resins. Both resin types may be successfully used with polyurethane foam, however.

Disadvantages

Cost. Epoxy resins are generally more expensive than polyesters due to a lower yield from raw materials charged into the reaction vessel and also due to the higher initial raw material cost. This tends to limit their use in volume applications except where their specific superior properties are required.

Toxicity. Use and processing of epoxy resins require well-ventilated areas, and almost all epoxy curing agents and hardeners are toxic or are skin sensitisers.

Cure. Although room-temperature cures for epoxy resins are almost complete, the resultant RP structures are not technically superior to those made using room-temperature cured polyester resins unless the epoxy structure is post-cured. At an elevated temperature and usually following a critical, rigid time-temperature schedule, epoxy cures are notably slower than those for polyesters. Hence, although convenient for tooling and other applications, the slower cure precludes extensive use of epoxies in large-structure, matched-die molding operations. Also, curing cycles are more critical for epoxies than for polyesters, and finished properties may be affected by the cure cycle as well as the type and amount of hardeners or other additives.[20]

Spray-up. Due to their toxicity, high viscosity and other problems, epoxy resins cannot be used in composite, resin-reinforcement spray-up systems as readily as polyesters.

Exotherm. Exotherm is propagated during cure of epoxy resins prior to the time that gelation occurs rather than after gelation occurs as for polyesters. In critical room-temperature curing applications, the increased temperature may result in resin runoff and air entrapment due to the lowered viscosity.

Wet-out. Epoxy resins have higher viscosities, hence trap more air and require longer wet-out times than polyesters. Epoxies also are not completely compatible with the sizing compositions on glass fiber that are normally available and used with polyester resins.

USES

Major uses for epoxy resins in Reinforced Plastics center around tooling (casting and laminating) and filament winding (wet winding and prepreg use). Many other uses exist such as flat laminating for electrical circuit boards (NEMA type), epoxy premix and powdered molding compounds. These will be further described in Section IX, on Design.

References

No.	Author(s)	Title or Periodical	Vol.	P.-Sect.	Year
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20	Anon.	Technical Bulletin A-15020, E. I. duPont de Nemours & Co., Inc.	—	—	1961
21	Anon.	Technical Bulletin "Epoxy Resins for Coatings," Jones-Dabney Co.	—	—	1958

Chapter III-4

FILLERS

INORGANIC FILLERS

Introduction

The following discussion was originally published in the 13th Annual SPI-R.P. Division Preprint Section 1-C, (1958) under the title, "Functional Inorganic Pigments for Use as Reinforced Plastic Fillers." The authors are S. R. Mountsier, Jr., and (Miss) A. J. Gitter, and the work was sponsored by Whittaker, Clark & Daniels, Inc.

Physical and Chemical Properties of Fillers

Anyone having experience with fillers in plastics will very quickly agree that these materials do far more than simply fill up space. For this reason, the term "functional inorganics" or "functional pigments" will be used in the following discussion. The term "pigments" is used by the paint field or surface coating field although basically the materials under discussion in most cases will not be used for coloring purposes. Actually, the term "*inorganics*" is probably most descriptive for the materials which will be discussed, since while these are essentially nonmetallic minerals, there are also a number of these inorganics used as fillers which are chemically precipitated and therefore cannot truly be classified as minerals. There are many cases where functional inorganics will give improved properties in Reinforced Plastics and their selection should definitely be based upon obtaining the greatest number of improved characteristics possible from the use of the functional inorganics. There are other cases where these pigments are used regardless of the fact that they may not be perfect but because cost, bulk or density or some other factor is of major importance.

The various resins and types of plastics change so rapidly that it is literally a physical impossibility for any company to be well acquainted with every new plastic material. It becomes (because of the man-hours required) an even more complex and impossible task to have a complete study of each functional inorganic pigment in relation to each of the resins and plastics available. The intent of this paper is to describe a variety of functional inorganics that either are being used in conjunction with Reinforced Plastics, or which conceivably could be used were their properties known to the plastic processor. Comparatively little has been printed as compared to the wide range of functional inorganics available as their various forms and grades.

In working with a wide variety of large laboratories, medium-sized Reinforced Plastic processors and small processors, one finds that there is a potential interest in a wide variety of functional inorganics. The materials which seem to be of interest are as follows:

- Aluminum oxide
- Antimony trioxide
- Asbestos
- Barium carbonate
- Barium sulfate (barites, blanc fixe)
- Bentonite
- Calcium carbonate (chalk, whiting, limestone, marble)
- Clay (kaolin)
- Diatomaceous earth (infusorial earth)
- Dielectite
- Feldspar
- Fuller's earth
- Graphite
- Ground glass
- Magnesium oxide
- Magnesium carbonate
- Magnesium hydroxide
- Magnesium trisilicate

- Mica
- Microsilicate
- Mullite
- Pumice
- Pyrophyllite
- Rottenstone
- Sericite
- Silica (flint, quarts, crystobalite)
- Slate flour
- Stearate—metallic soaps
- Talc (magnesium silicate, soapstone)
- Tellurium
- Titanium dioxide
- Tripoli
- Vermiculite
- Calcium sulphate (terra alba)
- Volcanic ash
- Earth colors (ochre, sienna, umber, red iron oxide)
- High-temperature calcined colors

Reviewing the above list, it is apparent that many of these materials are nonmetallic minerals which, of course, occur naturally. However, in certain instances there are chemically precipitated or manufactured forms of the natural materials which are listed such as blanc fixe and barium sulphate in conjunction with barites. In other cases such as magnesium compounds, these are essentially chemically manufactured.

Many times a processor, not being aware of the variety of grades available of a given functional inorganic, is apt to say that having tried a talc, a calcium carbonate, a clay, or a silica, that an inorganic is not suitable for his purpose without taking into consideration that there are many grades and many types of these various materials. (See Table III-4.1, p. 212.)

Of initial interest, however, are the basic chemical and physical properties of fillers. These are discussed below in a manner intended to clarify the points which are most often raised by processors desiring to use a filler material.

Particle Size. Most of the nonmetallic minerals are commercially prepared in standard grinds known as 200 mesh or 325 mesh. This grind or terminology generally infers 99% through whatever screen has been specified such as the 200 mesh or the 325 mesh. Obviously, there will be a gradual gradation in the particle sizes under this which is related to both the type of grind and hardness of the material during the grinding. Silicas, talcs, clays, micas, calcium carbonates and in fact, most of the naturally occurring functional inorganics are available in these screen sizes. For comparison, a 325-mesh screen is 44 microns.

The next general classification of materials would be those under 20-micron particle size. It is more difficult to prepare the natural minerals into a grade of this fine particle and generally either wet grinding or some form of jet attrition grinding is used. Typical of this particle size range would be some of the water-ground calcium carbonates as exemplified by "Atomite" or a jet-attrition-milled product such as magnesium silicate. It is comparatively difficult to obtain silicas in this particle-size range because of their abrasiveness on the equipment. However, there are exceptions but due to the difficulty in grinding, the cost generally increases.

The next range which should be considered would be under 1 micron where we find most of the chemically precipitated or processed inorganics. Examples would be magnesium carbonate, magnesium oxide, antimony trioxide and titanium dioxide. It is a general rule of thumb that natural minerals are most readily obtainable above 1 micron and the chemically manufactured inorganics below 1 micron. It could be mentioned that in processes wherein the inorganics are chemically precipitated, the inherent particle size is apt to be extremely low with the material itself oftentimes appearing coarser due to agglomerates created by drying.

There are several exceptions to the above statements, the most notable being neonovacite silica, which occurs in Arkansas. This material is a silica occurring in nature in an extremely fine particle size which can be separated by water levitation or air classification.

Reference should also be made to the colloidal or gel silicas and similar inorganics which are extremely useful tools as Reinforced Plastic fillers. Since these materials have been covered fairly often in the literature, little space will be devoted to them in this discussion.

To processors interested in Reinforced Plastic fillers there is not likely to be any interest in larger-sized materials but requests are frequently received for inorganic fillers in sizes well above 100 mesh ranging from pellets or pea size to fist size. When such a large particle of material is desired the most commonly thought-of fillers are products such as ver-

miculite, whitlite, pumice and similar low-density, lightweight inerts.

The second item of interest in these materials is *density* and *bulk*.

Density and Bulk. There is always the question of the relationship between fineness of particle size and bulk. Given the same material when it is more finely ground, there will be greater bulk. However, there are also cases such as the talc family wherein talc from different mines may be ground to the same particle size but still have a difference in bulk due to its inherent density. This is also true of the calcium carbonates and silicas. Materials having medium bulking properties would be calcium carbonates, clays, talcs and silica.

Oftentimes a bulky, low-density material is desired with or without a fine particle size. Vermiculite, whitlite, microsilicate and pumice would be typical. A material such as neonovacite silica would be bulky but somewhat heavier due to its inherent density.

In other instances, it is often desirable to give increased weight to a product and here attention is turned to materials such as barites, barium sulphate and blanc fixe, which even when finely ground, still have a comparatively low bulk and a heavy density which increase the over-all weight of the final product.

The third division by physical characteristics is color, which should be defined for these materials as transparency or opaqueness.

Color, Opaqueness—Transparency. Where a white color with maximum opaqueness is desired, selection should be made of the finest possible particle-size material with the highest brightness and the number one material under this heading is titanium dioxide. Due to the tendency of titanium dioxide to agglomerate during drying, one is often not aware of the extremely fine inherent particle size which lends to its white opaqueness when incorporated in a product.

Next on the list in giving whiteness with opaqueness would probably be antimony trioxide, with tin oxide and zinc oxide comparatively white.

In many products simply "good" average whiteness is sufficient and in this case selection can be made from the less costly materials such as mica, calcium carbonate, clays and talcs. All of these materials have a tendency to give some hiding or opaqueness. The mica, due to its particle structure, will often give a sheen that can be desirable and can be used to affect a brightness as might be created by opaqueness without the item's actually being opaque.

On the far side is the desire for materials with a tendency to give transparency. It is always a problem to incorporate a functional inorganic and fill to a maximum content and still obtain transparency. The silicas, microsilicate and ground glass have a greater tendency to give transparency than other inorganics. There is a considerable tendency to lose transparency as the particle size of the material is decreased. Where transparency is desired, the largest possible particle-size material should be considered.

Off-colored materials such as slate flour, soapstones, rottenstone and iron oxides are often selected regardless of color because of cost or even because they give better final physical characteristics to the Reinforced Plastic than can be obtained otherwise. These materials are also used as coloring ingredients.

Other organic colors are used for "coloring" purposes. The organic colors most often used need only be added in very small amounts and therefore do not enter consideration as functional fillers. However, it is often desirable to use earth colors such as red iron oxides, siennas, ochres or umbers wherein a sufficient quantity of the color may be used that it actually acts not only as a coloring agent but also as a filler.

A further group of colors which must be considered in relation to their filling properties as well as their coloring properties are the high temperature, inorganic colors as typified by cadmium-selenium reds. Here, where the final shade to be obtained is dependent upon the amount of color which can be incorporated, and since these colors inherently have considerably less hiding properties and tinting strength than the inorganics, their role as fillers must be evaluated in any system in which they are used. The importance of the high-temperature inorganic colors is increasing, particularly for electrical applications where *in-service* temperatures or where forming temperatures would destroy the organic colors. This type of color is suitable for use up to a minimum of 1500°F without bleeding or sun-fading and is generally quite resistant to acid and alkalies.

An important characteristic is the ease of mixing or incorporating in a batch, known as *dispersion*.

Dispersion. The ability of the various inorganic fillers to disperse is basically related to the surface tension of the material but other factors such as fineness of grind, and method of incorporation will influence their ability to disperse. Clays, calcium carbonate and silicas all wet easily and tend to be easy to disperse. Micas, graphite and the more slippery talcs may be somewhat more difficult to disperse but in general the finer the grind, the easier is the dispersion problem. This can also be influenced by the order in which the ingredients are added to a batch and considerable help in dispersion can often be obtained by changing the order of mixing.

Thermal Behavior. This is the fifth characteristic to be considered. Thermal conductivity and thermal expansion, which are quite distinct, are important. Ideally, there should be a material available which would expand permanently at comparatively low temperatures so as to counteract the shrinkage of the plastic resins. There are materials available which, at high temperatures such as 1000°C, do expand and retain their expansion even after cooling. This is generally caused by a high formation of the crystal mullite which has a very low coefficient of thermal expansion at all temperatures. The same is true of vitreous quarts, calcined alumina and certain forms of silica mineral such as calcined diatomaceous earth. It must be recognized that in a system it is seldom the functional inorganic particle which shrinks at the working temperature. It is rather the shrinkage of the plastic resin which pulls the inorganic particles closer together and conceivably even shifts the physical position of the finer particles, giving a tighter and more dense packing of the mass.

The thermal behavior of the inorganics during forming is of less concern possibly to Reinforced Plastic fabricators than to other processors where increasingly, temperatures up to 600 and 700°F are being required for forming. Here, attention must be given to the presence of chemically or mechanically combined water which might start to be driven off. In general, all of the "oxides" group are good for forming at temperatures up to 700°F.

For most applications, the decomposing temperatures of materials such as calcium carbonates and calcium sulfates are not a factor, as these are generally well above the life of the plastic resin. In a few cases for electrical work, consideration has to be given to behavior of the filler at extremely high temperatures. Where there might be arcing, it is advisable to review the melting and softening points of the inorganic pigment and to pick a material which softens rather than decomposes.

In general, most inorganics are still selected wanting a low coefficient of thermal expansion over the span of the temperature range of the plastic filler. There are instances where a material having a high coefficient of thermal expansion could be desirable. For example, if there is a plastic-to-metal seal, and under service conditions the metal expands, it might be desirable to have the functional inorganic expand also. While not in the Reinforced Plastic field, an example would be a resin-bonded mold for investment casting where a material such as crystobalite is used as the major filler. Crystobalite, being a form of silica, has a sharp coefficient of thermal expansion at 250 degrees C, and by adjusting the percentage of crystobalite, it is possible to somewhat adjust the thermal shrinkage of the mold to match the coefficient of expansion of the metal or alloy.

The thermal conductivity of the inorganic fillers is important again, when using them for insulation purposes. It may be desirable to have a material with a low thermal conductivity such as asbestos or to have one that has a high thermal conductivity as Al_2O_3 so as to maintain a cooler in-service temperature on the finished product. Hard calcined magnesium oxides, silicas and powdered metals would conduct the heat away most rapidly.

Electrical Properties. Unfortunately, the cost of the equipment alone for making measurements on "Q" factors and dielectric loss are expensive. This cost, combined with the complexity of the available materials to be evaluated, has limited research, so comparatively little statistical information is available. Micas are the old standby and well-known filler where electrical properties must be watched. Silicas follow them closely. Atomized aluminum, which by its formation carries a coating of aluminum oxide on each particle, takes advantage of the good electrical characteristics of aluminum oxide. It would seem logical that the plastic industry should evaluate the materials which the steatite-insulator people and the spark plug manufacturers use to obtain their good electrical properties. In this group are steatite talcs, magnesium oxide, and "Forsterite." Far more work needs to be done to determine which are the best materials at this point. What may or may not be an anachronism is the relative effect of alkali present in the inorganics. The

steatite-insulator people have found it desirable that the alkali be extremely low. Electrical applicators of Reinforced Plastics have found micas to be very satisfactory and micas are high in alkali.

As yet, the plastic processors have not been confronted with the problem of functional inorganic fillers which might tend to lose electrical properties as the temperature in-service increases. However, in time this too will be a problem that must be faced. Here, under some conditions, we find that a material such as titanium dioxide which is a comparatively poor electrical insulating filler at low temperatures improves its electrical properties at higher in-service temperatures.

Mention must also be made of the availability of materials that are conductors of electricity such as magnetic iron oxide. To us it is even conceivable that the present ceramic ferrites might someday find competition from magnetic ferrite particles which are bonded together by plastic resins.

Suspension. The ability of a functional inorganic to stay in suspension is related to its particle size, its particle shape, its inherent density, the viscosity of the suspending vehicle, and the pH of the system. The same material may suspend in one system but be very poor in another system. In general, the finer the particle, the flatter the particle shape, and the lower the density, the better the material will stay in suspension.

Particle Packing. To obtain the best particle packing, there probably is no answer other than "Edisonian Research." The same principles used in getting maximum density from concrete (where the fine particles of the cement are mixed with the coarser particles of the sand and gravel) are true with fillers. Figures have been worked out by the concrete industry and by ASTM showing the ratio of coarse to fine particles desired to give the best packing. However, there is no rule that will tell the fabricator that for a given piece to have a final specific size and shape, the top particle that can be used as a filler is of such and such a mesh or micron size. Due to both internal and external stresses caused during forming and curing, there is apt to be a difference in the most desirable particle sizes used even with the same plastic resins for different size pieces. From practical experience, the fabricator will learn that certain types of edge cracking, laminations and stresses can be relieved by using a coarser or a finer particle.*

Industries seem to go through phases and currently more inquiries are made concerning materials having the ultralow micron size ranges. Because the coarser particles tend to settle out, they are sometimes disregarded when they could become a very significant factor, if properly handled, for decreasing shrinkage, for relieving internal strain and to obtain maximum loading where it is desirable. Quite conceivably the knowing fabricator will use graded particle sizes of the same filler to obtain best results. Unfortunately, the grading of the particle sizes increases the cost of the fillers but as a working tool, it could be invaluable in reducing losses.

Ion Concentration—pH. In general, consideration is given to the pH of a system as pertains to the plastic resin being used. However, the pH will affect the functional inorganics and where some manipulation is possible within a system, it is quite conceivable that certain of the functional inorganics could be used to advantage by varying the electrolytic action on them. For example, clay, when in an alkaline system, will be deflocculated and become quite viscous. However, an excessive amount of alkali can make it overdeflocculated and turn watery. By the same token a slight acid condition with a clay will flocculate it and an excessive acid condition can cause thixotropy.

Talcs and silicas are not quite as sensitive to changes in pH as the clays. Also, there is the phenomenon of materials that may continuously be slightly soluble and if shelf life has been involved, could materially affect the system.

At the same time, this continuous solubility of some of the inorganics can be used for beneficial effects such as a magnesium carbonate which will keep a liquid system on the alkaline side over a long period of time.

Mention might also be made of the finished product which has to stand a test of water immersion after being completed and wherein slight water solubility of the filler could cause a change in electrical properties or other characteristics important to its use.

* Note: Maximum particle packing occurs with following distribution: 40% coarsest particles (baseballs), 40% finest particles (sand), 10%—medium particles (golf balls), 10%—medium particles (acorns).

Particle Shape. There are more theories on the effectiveness of particle shape than actual knowledge. With the event of the electron microscope and its more ready use, we are finding that many of our theories and nomenclature used to describe particle shape and characteristics are erroneous. However, we can safely state that there are certain general classifications which seem to be specific beyond question. Of these, undoubtedly the most distinctive would be the fibrous characteristic of asbestos and of man-made glass fibers.

The term "asbestine" was coined as a trade name to describe a tremolotic, talo-like mineral having a long particle, yet definitely one that could not be described as fibrous in the sense that asbestos is fibrous.

The next deviation by nature from this long tremolotic particle as found in calcium silicate and the truer tremolites (talc) and the needle-like particles or crystals of kyanite and sillimanite which convert into mullite upon calcining at high temperatures.

There is no question that under certain conditions the fibrous type particles will give an interlocking reinforcing characteristic and there is reason to believe that the long, needlelike particles of certain inorganics can have advantages.

Flat, plateylike particles are commonly recognized when appearing as mica. Certain talc formations such as in Vermont and the South will have the same type of platey particle. It has long been recognized that the platey characteristic of mica and of the selected grades of talc gave good suspendability. A more interesting feature about this type of particle is that when used in small amounts with other inorganics, it can give an elasticity or flexibility which, in certain types of formulation, tends to reduce small cracks and to help release physical strains created by changes in thermal expansion up to 200°F.

Recent work has shown that a number of clays are predominantly flat, hexagonal crystals. This, in addition to their predominantly fine particle, can be a contributing factor in their ability to suspend in liquids.

Definite crystal shapes and cryptocrystalline particles are common in most inorganics if we have the proper magnification for seeing them. In general, since the inorganic fillers as used are well below 325 mesh, it is difficult to see the exact crystal structure. Most calcium carbonates, barites, feldspar, and certain silicas would show crystal formation under an electron microscope. These inorganics when mined will show only small crystalline formation and to those not familiar with minerals, probably 75% of all the materials mined would appear to be simply massive and nondescriptive.

About the only mineral which is available having a truly round particle would be sands that have been washed and rewashed until their very abrasiveness upon each other has formed the rounded particle. Glass beads are likewise available with a round particle but are comparatively expensive.

The term "massive" is often used to describe the physical characteristic of a variety of materials and especially of a number of talcs. This term seems to be most applicable for those materials where the crystal formation is so incomplete or indecisive that there is no specific structure.

The term "amorphous" has long been used in describing various functional inorganics and while it is currently widely misused, there is a need for a word to describe the materials which we formerly described as amorphous but which we now know simply have such a superfine crystal formation that it is not readily seen. Chalks, soft silicas, opal would be typical of materials described as amorphous.

Powders prepared by grinding a material that is in a solid state are also used increasingly. Ground glass would be the most outstanding example of this with vitreous quarts being a second example.

Particle shape in general is a characteristic widely discussed in relation to its behavior as a functional inorganic but there is reason to believe that probably a wider variety of materials ground to identical particle-size distribution curves with comparable true densities would behave essentially the same way as fillers and that until we have more specific knowledge on the inherent particle shape as distinguished from the apparent particle shape, we may be following false theories as to the "why" of the behavior of a given material.

Inertness. Essentially all of the functional inorganics are classified as inert. None of these materials will burn nor will they support combustion. Likewise there will be no fundamental change in the chemical properties by temperature itself up to 200°C with the exception

of mechanically combined water which will be driven off.

It should be noted that a difference is made between mechanically and chemically combined water in that the former is the moisture that can be driven off by oven drying.

The chemically combined water, which is shown in most analyses as ignition loss, is a matter of consideration for products which must tolerate high in-service temperatures.

In general, the silicas and silicates are inert to both acid and alkali. Typical of this would be talc, clay, asbestos, feldspar and flint.

The carbonate group such as calcium carbonate and magnesium carbonate obviously would not be resistant to acid but would be resistant to alkali.

The picture on the oxides is fairly complicated in that if the oxide has been calcined at a high temperature, it will be chemically resistant to both acid and alkali; examples: aluminum oxide, mullite and titanium dioxide. Magnesium oxide, being more difficult to calcine at a sufficiently high temperature, sometimes has a tendency to rehydrate. The chemically precipitated materials, due to their inherently finer particle sizes, are apt to be slightly more soluble or rather to have slightly more effect upon the ionic concentration of a system than the natural minerals.

Chemical Analysis. The functional inorganics generally classified as carbonates are the calcium carbonates (whiting, chalk, marble), magnesium carbonate (dolomite, magnesite), barium carbonate (witherite) and so forth. All of these are widely used as fillers in Reinforced Plastics but due to the potential evolution of the CO_2 and the corresponding decomposition of the filler, they are normally selected for use where the in-service temperatures will be under 500°C.

The silicates, which form the biggest bulk of inorganics used as fillers, include such materials as talc, clay, asbestos and feldspar. They are popular because of their physical characteristics, chemical inertness and comparatively low cost.

Oxides are also of great importance as fillers, the most common being silica. Alumina, titanium and magnesium oxides also have an important place as fillers.

Using the term "synthetic" as distinguished from precipitated or chemically processed covers a wide variety of important materials. In this classification we would include fiber glass itself, glass, mullite, synthetic talc, synthetic forsterite, microsilicate and whitlite.

In general, the hydroxides and the sulphates have not proven as popular as fillers for Reinforced Plastics as the other materials. There is a definite place for calcium sulphate in certain products where its characteristics of "bringing up colors" could be utilized.

Absorption—Adsorption. These are properties of great importance to the filler user. Materials such as diatomaceous earth, clay and pumice will have high absorption as can be seen by their oil-absorption indexes. Other materials such as silicas and mullite have low oil absorption. There is a correlation between fineness of grind and absorption; the finer the grind, the higher the absorption. However, two inorganics of the same fineness of grind but made from different qualities of ore will have different absorption characteristics. Certain inorganics will have greater tendencies toward adsorption than others and this seems to be related to the true surface area and the surface tension of the material.

Obviously, where it is desired to increase the viscosity, a material having a high absorptive characteristic should be used or one having a finer grind. Conversely where viscosity must be reduced then the coarser grind or the lower absorbing materials are suggested.

Absorption is also related to the type of the particle in that some materials such as diatomaceous earth have a continuous capillary cellular structure. Microsilicate on the other hand has a discrete cellular structure and therefore less tendency for high absorption than the diatomaceous earth. Silicas, by further contrast, have no cellular structure and therefore tend to have a low absorption. There are also some products in which the lattice structure is adjusted so as to give adsorption and a corresponding high viscosity or suspension such as the "Bentones." Treatments such as amine coatings render fillers non-oil-absorptive, and also reduce laminate water absorption.

Forming Aids. Often materials are used to give internal lubrication or lubrication during forming such as the stearates and certain of the low-micron inorganics. Low micron mica, magnesium silicate and sericite often function as lubricants in addition to having filling characteristics. In both pressing and extruding, the ability of this type of material to give increased flow or lubrication is often highly important in

securing a good surface and high production runs.

Cost. To many users of the functional inorganic fillers the problem of cost is more important than physical and chemical characteristics. In many cases these functional inorganics are used as a means of decreasing the over-all cost and extending the dollars of finished products obtainable from the more expensive resins.

There is a sizable group of inorganic functional fillers available ranging in cost from ½ to 1 cent per pound. This group includes slate flour, silica, dry ground clays, dry ground calcium carbonate, soapstones, inexpensive off-color talcs and comparable fillers. In general, their color is somewhat poor although there are surprisingly good white materials available within this group. For the most part, these materials will be in the 200 to 325 mesh category.

Increasing the allowable cost from 2 to 5 cents per pound, it is possible to obtain far better control on color and screen size with an increasing number of materials available in finer particle sizes. Here again, we find silica, low micron slate flour, wet ground calcium carbonates, water levigated clays and both steatite talcs and low micron talcs.

In what might be called a medium cost range of 6 to 15 cents per pound, we find a different range of materials with color, micron size, oil absorption, bulk and similar factors more specialized and the product more carefully controlled. Again silicas occur, only now we find them available in graded particle sizes like coated calcium carbonates and the highest brightness, jet attrition microsilicates. Also, within this group are the materials such as pumice, diatomaceous earth and microsilicate which can pass either extreme fineness of size or can have exceptionally high bulk and are characterized by their low density.

Within the high-cost field of 20 to 50 cents per pound we find the available materials growing smaller and an increased number of the synthetic products occurring, such as synthetic forsterite, synthetic talc, mullite, neonovacite silica and the still more closely graded materials as to particle size.

Above the 50 cents per pound range we have still a further group of materials used by the Reinforced Plastic fabricators as fillers, which includes the silica gels and other specially prepared inorganics.

Conclusions

It is quite obvious that the Reinforced Plastic processor must select from a wide variety of physical and chemical properties to determine which fillers will give the final characteristics most important to him. Next comes the job of fitting the functional inorganics into this pattern. There are many cases in which one given inorganic will satisfy all requirements. However, there is reason to expect that within increasing experimental work the Reinforced Plastic processor will incorporate perhaps several functional inorganics of distinct compositions or perhaps several qualities of one of these materials having perhaps different particle-size distribution curves in order to obtain the final desired results.

All of the materials that have been mentioned in this paper are commercially available in sizable quantities. In time, undoubtedly, there will be many functional inorganic pigments or fillers produced specifically for the Reinforced Plastic field and their production will be the outgrowth of the demands made by the fabricators to obtain a more truly functional behavior from the filler. (See Table III-4.1, p. 212.)

FILLERS FOR SPECIFIC RP APPLICATIONS

Introduction

In addition to the general listing of fillers in the previous discussion, inclusion of the detailed functions of specific fillers in several diverse RP applications is desirable. Because fillers alter RP properties in so many ways, close investigation has been made of those regarded as most important, and the most logical categories have been created for discussion of these properties.

The most important functions provided by fillers in RP processes are: lowering of exotherm, reducing resin cost, modifying mechanical and surface properties, and providing a base for color effects.

Clays vs. Calcium Carbonate

Clay or calcium carbonate fillers are widely used in mixes for matched die molding, with loadings up to 40% being possible, but with the optimum loading at about 25%. Although clays are probably used in a greater number of applications, strength tests on matched-die molded panels comparing the two materials showed no essential difference in physical properties. It was concluded that the effect of either

filler on physical properties was not as important as its effect on stability (pot life), handling properties, flow, and molding characteristics.[3]

For most of the materials commonly used as fillers, including the calcium carbonates, the same general particle shape exists through the entire finer particle-size range. Hence, properties to be expected from the various particle sizes of these materials are generally predictable, since the properties are governed by the same surface area and packing relationships.

With kaolin clays, however, particles less than two microns across exist as thin flat hexagonal plates that are approximately one-tenth as thick as their nominal diameter. Kaolin particles larger than two microns exist as stacks of these plates so firmly bound by natural forces that they act as single particles and cannot be separated into the individual plates by grinding. Hence, grades of clay containing a large percentage of plates are governed by different surface area and packing relationships than grades containing a large percentage of stacks.[4, 5]

The finer particles tend to increase the viscosity of a resin-clay mix, while the larger particles are desirable for reducing both shrinkage and crazing. Only extra-large particles must be avoided because of the action of glass reinforcement in screening them out during molding, thereby creating discolored lines and adjacent areas of resin richness.

Incorporation of clays and/or calcium carbonate was found to specifically improve matched-die molded parts as follows:[6]

1. Eliminated crazing and excess shrinkage especially in step areas.

2. Gave a smoother, denser, full-bodied surface with increased barcol hardness and eliminated porosity; molded parts had good eye appeal.

3. Pigmented parts improved appearance, permitted duplication of paint colors and replacement of painted metal parts with colored moldings. Color pigment costs were nil due to the bodying effect of the fillers.

4. Usual crazing of molded polyester parts in a postbaking cycle of 15 to 20 minutes at 400°F required for a painting operation was eliminated by incorporation of up to 40% filler.

5. Cost per cubic inch of resin mix was reduced 18% by filler addition with no bad effect on laminate physical properties.

6. Wet strength was affected as follows (35 to 40% glass);

	No Clay Filler	40% Clay Filler
Dry flexural strength	26,500	28,100
After 14-day immersion, H_2O	16,000–19,700	21,400–23,720

Certain coatings such as amine types may be applied during original processing to kaolin clays to reduce oil (hence resin) absorption.[4, 7] Such modification will deflocculate the clay particles (average 0.77 microns diameter), and permit rapid and thorough mixing and a higher degree of dispersion in the resin than is possible with untreated clays; also, no effect on pot life, cure time, or exotherm rate is reported. Untreated clays may absorb promoters or catalysts, and thus adversely affect gel and cure times.

Following is a tabulation of results of tests on both resins and laminates made to compare the additional benefits of treated over untreated clays. A general-purpose polyester at 10 poise viscosity was laminated with 25% glass in preform moldings and 10% glass in premix parts. Clay contents were varied as indicated.

Test or Property	Untreated Clay	Treated Clay
Preform Molding Mix, Viscosity Change, Poise:		
25% clay	30	15
40% clay	350	40
Flexural Strengths, psi:		
Preform, 30% clay	32,800	34,000
Preform, 40% clay	23,800	34,800
Premix, 40% clay	11,500	12,600
Glass-Resin Bond Strength	No noticeable difference	No noticeable difference
24-Hour Water Absorption, %:		
Preform, Type I clay, 40%	0.24	0.17
Preform, Type II clay, 40%	0.35	0.27
Premix, Type II clay, 50%	0.76	0.55

In actual molding plant practice, surface modification has not always proven 100% essential, and both untreated and treated clays are used.[6]

The procedure for adding clay to a resin production-batch mix is: (a) weigh resin at 25 to 30 poise viscosity into a large (50 to 250 gallon) container; (b) using a 6- or 8-inch diameter mixing blade or propeller type paddle (two on shaft), stir at 300 to 400 rpm and add clay slowly, mixing for 50 minutes; (c) add catalyst dissolved in styrene or other monomer sufficient to reduce viscosity to 8 poise (without filler) for molding, and mix 10 additional minutes; (d) allow the mix to stand for at least one hour to permit air voids to rise to surface. Less air is introduced through a deep vortex if the resin is more viscous during mixing; hence, less air is dissolved in the resin. Care properly exercised in handling clay filler will assist in eliminating many of the defects associated with surfaces of matched-die molded parts.[4, 8]

Clays or calcium carbonates are also used separately or in combination in polyester premix molding compounds. Better electrical properties but higher shrinkages after molding are favored by use of clays. The shrinkage is greatly reduced but electrical properties are also made poorer by the use of calcium carbonate. Loadings of the clay or calcium carbonate filler approach 55% in premix.

Test procedures for accurate measurement of particle-size distribution in fine materials are available from material suppliers. The best method for determining particle size of a filler when dispersed in a polyester resin is by use of a Hegeman draw-down gauge.

Viscosity Control

The following problems in RP are greatly contingent upon resin flow characteristics and effectiveness of fillers in controlling such flow: runoff of resins used in hand lay-up and spraying (including gel coats), control of resin viscosity in matched-die molding mixes when heat is applied during mold closure; control of viscosity to eliminate heat build-up during mixing, and prevent resin-filler separation during molding in both premixes and potting and encapsulating compounds.

Degree of flocculation, or mutual attraction between particles of filler is disturbed during agitation, as with a clay mix, and reasserts itself after mixing when the system again becomes quiescent. Hence, a matched-die molding mix containing clay will thicken after mixing. However, additional nonflocculating materials, such as the finely divided silicas usually produced from a vapor phase, (flame hydrolysis), have particles less than 0.5 micron and are irregularly shaped so that mechanical interlocking actually occurs. Quantities of 1 to 2% of such silica fillers alone in a hand lay-up or spray-up resin will prevent runoff after the resin, even in agitated viscosities of three to five poise, has been applied to the reinforcement. Quantities over 3% will produce jelly or vaselinelike mixes, hence presence of the silica thixotropic agents is also desirable in gel coats, although other extenders including clay and coloring pigments are also used.

Ways of measuring the effectiveness of thixotropic agents in thermoset resins are:

Drop Method. One or two cubic centimeters of resin containing the thixotropic agent is placed on a smooth glass plate inclined at an angle of five degrees from the vertical and rate and amount of rundown compared to that for an equivalent quantity of clear resin. Temperature must be accurately controlled at 70°F. This test may also be conducted by impregnating the fiber glass cloth, mat or woven roving actually to be used in the work, and observing runoff with the glass plate at the same 5° angle.

Brookfield Viscosimeter measurements may be taken with the appropriate spindle revolving first at *low*, then at *high* speed. The thixotropic index is determined by:[9]

$$\frac{\text{apparent viscosity at low shear}}{\text{apparent viscosity at high shear}} \qquad (1)$$

Index values range up to 5.5.

Vibration mechanisms such as an eight-ampere "Syntron" (3600 cycles per second), or a vibratory sanding device (SKIL Model 438) are mounted under the resin container and Brookfield Viscosimeter or Extension Rheometer spindles mounted in the resin mix. The vibratory action rapidly reduces resin viscosity in an amount proportional to the amplitude of vibration. Hence, the viscosity index range can be extended to 10 to 1, and flow properties of mixes containing higher amounts of thixotropic filler can be evaluated. Vibration of nonfilled resin produced no viscosity variation.[9]

Thixotropic properties in matched-die molding mixes are of value in creating a back pres-

sure during molding until the force of the closing die overcomes the shear strength between particles, thereby preventing resin-filler separation. It is also desirable to avoid an excessive amount of coarse particles, thereby preventing settling.

In premix molding, asbestos 7TF-1 floats (present at 7%) are probably the most significant factor in controlling the fluidity of the premix compound during its preparation. Clays and the general high filler loading contribute to the resistance to flow during molding. Clays and calcium carbonate also cause trouble due to lack of perfect homogeneity with the resin when mixed, however, because separation does occur during molding. The resin, being reduced to waterlike viscosity due to heat of the mold, will run ahead of the filler and reinforcement, permitting separation and resin-rich areas.

This has presented a serious problem in polyester premix molding, and shows signs of being overcome when the amount of glass reinforcement is increased to 35%, a high-temperature catalyst (*t*-butyl perbensoate) is used, and the mixing is carried out in a heated compartment at 130°F.[7]

Low thixotropy is usually maintained in potting and encapsulating compounds since high fluidity and escape of bubbles is desired, and they are generally poured into a confined container and allowed to cure. Sealing compounds require some thixotropy to prevent runoff. Pulverised sand constitutes the major portion of the filler, and the loading is high, since freedom from shrinkage is desirable.

Abrasion

Abrasion-resistance in RP parts may be induced by incorporating a nylon cloth to which silicon-carbide granules have been adhered. Such a surface on an RP part reportedly provides abrasion resistance greater than that for glass cloth by a factor of ten and equivalent to or better than an aluminum metal surface.[8] Finely-powdered alumnia and silicon carbide as surface-coat fillers also provide abrasion resistance, such as for tooling work.[9] Addition of sand grains (10 to 20 mesh) to a gel coat provides a finished, slip-proof and non-skid surface for boat decks and swimming pool aprons. The sand used should be completely dry and free from grease or oil.

Addition of metal powders to resins does not contribute in any way toward improving resistance to abrasion.[10]

Metal Fillers

Powdered metal fillers exert an influence similar to that for metal wire and mesh reinforcement in RP, i.e., rapid dissipation of exotherm and also external heat, elimination of strains, conduction of electricity, etc.

Metal fillers have been used in epoxy molds which were rapidly cycled between 160 and 240°F.[7] Electrical-heating and water-cooling coils were imbedded, and great versatility in casting (no viscosity increase), manipulating, and repairing the molds were possible.

Aluminum (66% loading), zinc, copper and steel (80% loading) are possible additions to epoxy resins. Ultimate properties closely duplicate those of the original cast resin, except for small increases in thermal and electrical conductivity, and large gains in specific gravity.[11]

Care must be exercised in use of metal powders with polyesters due to the effect of metal ions in providing free radicals, reacting with inhibitor, or otherwise functioning to promote rapid cure. It is desirable to make metal powder additions to polyesters directly at the time of use, and not permit more than several minutes' contact time prior to cure.

Fire Retardancy

Additions of 5% antimony trioxide (fine powder) to any of the class of fire retardant polyesters containing HET acid reduce the Underwriters' Fire Rating from 60 to 70 (for unfilled HET acid resin) to 20 to 25, and qualifies the cured parts as self-extinguishing. Calcium carbonate or calcium sulfate are usually also included as auxiliary fillers together with the Sb_2O_3. However, it has been found that fine-powdered (200 mesh) natural magnesium carbonate (not precipitated grades containing chemically held water) is more desirable as an auxiliary filler for the Sb_2O_3 because the $MgCO_3$ decomposes at approximately 660°F. This temperature is safely above the curing (peak exotherm) temperature of the polyester, and well below the combustion temperature (1300 to 1700°F). It is also below the decomposition temperature of calcium carbonate. The $MgCO_3$ functions as a flame snuffer by releasing carbon dioxide starting at 650°F. Loadings up to 40% by weight are possible, but mix viscosity increases radically for additions above 20%. Fire-retardant ratings were reduced to 8 (radiant panel) for 5% Sb_2O_3 + 20% $MgCO_3$ in a HET acid resin.

It is desirable to maintain a maximum total styrene addition not above 15% in polyesters intended for fire-retardant applications. In spite of low fire ratings, smoke density is generally at a level high enough to preclude code approval for use of polyester-fiber glass structures in many building applications, especially interiors.

Epoxy resins formulated with diglycidyl ether of tetrachlorobisphenol A, and cured using chlorendic anhydride as hardener (100 phr) fall in the fire-retardant category.[6] Addition of 5% antimony trioxide is also desirable.

Antimony trioxide included as filler in heavily chlorinated thermosets chemically combines with the chlorine to form SbOCl which, in turn, is easily decomposed and acts as a flame snuffer. Antimony trioxide is non-light-fast and yellows slightly with age, however.

Phenolic resins tend to burn slowly or not at all. Several types of phenolics may be rendered fire-retardant and self-extinguishing by the incorporation of dicyandiamide.

Additional fire-retarding potential may be built into reinforced thermoset resin structures by the addition of 5 to 10% of a finely divided, rigid polyvinyl chloride. No curing or gel time irregularities result, and the PVC material, being a white powder, is free from color and also imparts good light stability. Loadings above 10% substantially increase the viscosity of fluid resin batches, however. Discussions of additional means for incorporating fire retardancy into plastics may be found elsewhere.[12]

Low-Density and Bulk Fillers

Microspheres. Phenolic, ures-melamine, glass, high silica glass, and pure silica as hollow spheres are made by a proprietary process[13] described as "spray drying" a mix of resin, solvent and dissolved gas (N_2),[14] or, for the glass spheres, compounding a batch and "ballooning"[15] through a furnace and cyclone separator.[16]

"Syntactic" (great uniformity of construction) foam materials are formulated by mixing the plastic spheres together with various resins (epoxy, polystyrene, and silicone resins, and inorganic silica sol) to provide materials with qualified electrical properties for use in electronics. Similarly, the glass spheres are mixed with epoxy resins and various other matrices to produce composites also for application in electronics.

The spheres themselves (plastic or glass) range between 10 and 300 microns in diameter, are hollow and have a wall thickness of approximately three microns. Bulk density of the phenolic spheres is 3 to 5 pounds per cubic foot while that for the glass spheres is 14 pounds per cubic foot.

The phenolic beads in an epoxy matrix have been used for patching wood and various aircraft structures, and also to form low-density pattern boards for tooling applications.[17] Care is required in mixing and molding to avoid separation of resin from the spheres.

Cured pattern-board material is completely isotropic with no grain or fibrous content to cause more water absorption or differential expansion along one axis than along another. The material may be sawed, carved, nailed, laminated-to, or otherwise processed like lumber. It is a highly desirable material because of lightness of weight and dimensional stability.

A listing of typical properties of this material is of interest:

Cured density	40–45 lb/cu ft
Ultimate tensile strength	1,600 psi
Ultimate compressive strength	7,000 psi
Compressive modulus of elasticity	90,000 psi
Compression deformation	35%
Ultimate flexural strength	3,000 psi
Flexural modulus of elasticity	140,000 psi
Water absorption (2-hr boil)	>3.0%
Volume resistivity, −75°F	5×10^{13} ohm/cm
Dielectric constant, 60 cycles	3.6
Dissipation factor, 60 cycles	0.061

The glass spheres by themselves possess the following properties:[18, 19]

True density, gm/cc	0.3
Bulk density, lb/cu ft	14
*Temperature stability	1000°F
Compressive strength, psi	2500
Thermal conductivity (Btu/sq ft/hr/°F/ft)	0.02
Water absorption, 24 hr	5.0%

Inorganic Hollow Beads. Development has been made of a lightweight, hollow, inorganic bead material which, when mixed with aluminum powder and silicone or phenolic resins pro-

*Note: Thermal stability of the ceramic spheres is 3000°F.

vides high-temperature operating and thermal shock-resistant structures with the following properties:[28]

	Flexural Strength		% Ret.
	Room Temp	750°F	
Beads with silicone resin	30,000 psi	10,000 psi	33%
Beads with phenolic resin	45,000 psi	28,000 psi	62%

Inorganic laminates were also made using sodium and potassium silicates with the hollow-bead fillers. Silica sols, oxysulfate and oxychloride cements, calcium aluminate cements and phosphate cements were used as bonding agents or matrices. Protective coatings for such reinforcements as fiber glass, asbestos and refractory ceramic fibers were applied to prevent attack and weakening due to the alkalinity of some of the cements. This procedure resulted in laminates with flexural strengths of 11,000 psi at room temperature and 10,000 at 750°F.

The prime intended application of the inorganic hollow-bead laminates is in radome structural materials for operation about 500°F.

Other low-density, bulky inorganic fillers may be used in RP. These comprise lightweight ceramic aggregate, amorphous mineral forms such as tripolite, diatomaceous, or infusorial earth (silica, perlite), and other amorphous varieties classed as oolitic (limestone), pisolitic (bauxite), and the heat-expandable mica, vermiculite.

It is generally difficult to incorporate all the desirable characteristics into an RP laminate or sandwich structure, and the practice has customarily been to sacrifice strength for the purpose of obtaining low density, and vice versa.

Bulk Fillers (¼-inch dia. and larger). In casting stretch dies and other large-size tools for shaping such parts as airplane skin panels, accurate surfacing and freedom from warping are prime requisites. Use of medium-to-large quartz pebbles, granules, or limestone rock aggregate in clay-filled epoxy tooling plastics will reduce both shrinkage and maximum exotherm temperature. By this means, it is not uncommon to cast large forms with dimension contraction (after curing and cooling) of less than ½ inch in a 13-foot span or length. Some of the castings containing rock aggregate approach 6000 to 7000 pounds total weight. Forms so cast using epoxy resin and rock aggregate are much stronger than Portland cement forms. In fact, the only similarity is in use of a cement mixer to prepare the epoxy-stone mix.

Economy in use of resins is realized also, because use of rock aggregate permits total epoxy resin contents as low as 9 to 11% in the tooling formulation.[29] Other large-sized aggregate materials which have been used are: silicon carbide or aluminum oxide granules; lumps or coarse grains; glass or porcelain marbles; expanded popcorn; and miscellaneous organic or inorganic aggregates which preferably do not absorb the resinous binder.

The best of those evaluated with the above, a porous volcanic aggregate, gave the following properties at 80% loading in an epoxy tooling resin:

	¾ inch Dia. Aggregate	¾ inch Dia. Aggregate
Compressive strength, psi	1900	1000
Average density gm/cc	0.88	0.64
Crushing strength, psi	3400	2100

A simulated aged appearance may be induced into surfaces of RP parts to create "synthetically weathered" architectural components, masonry, sculpture, statuary, etc.[30] Rock salt of varying granular size (¾ inch and smaller) is cast or molded into the surface, and is washed away with water after cure has taken place. Unique appearance effects may be thus produced. Water-soluble crystalline salts other than rock salt may also be used to vary size and shape of the "weathered" surface indentations.

In addition to its use in nonskid RP surfaces, sand may also be used together with inorganic coloring pigments to produce panels used as exterior siding and simulating natural stone.

The panels may be produced in close-fitting, easily handlable modular units with deep-raked joints, and are nailed in place over conventional siding.

High-Temperature Fillers

Graphite is used as a filler to provide RP laminates which conduct electricity, bleed off static, etc.[31] Graphite is also used in thermally resistant and ablation-resistant resin structures, and provides thermal end points to 5700°F in a phenolic resin structure. (Graphite sublimes at approximately 7000°F, and hence, has an upper practical thermal operating limit of 6600°F).[32] Because graphite-loaded reinforced laminates are brittle, thermal resistance and strength must be combined by providing such constructions as graphite-filled resinous surfacing over ceramic or high-silica, fiber-reinforced substrates. Many such combinations are possible and are governed by cost, ultimate mechanical or thermal requirements, etc. (see Section III, Chapter 3, Miscellaneous Reinforcements).

A water-dispersed graphite filler has been used under clear resin as a coating applied to a prepared form to produce a surface-heated mold.[33] The clear, protective coating was placed over the conductive layer, but electrodes were incorporated to carry current to the layer. A power input of 0.75 watt was desirable in using the surface-heated molds to cure RP parts, inducing a temperature of approximately 240°F.

Organic Fillers

The various substances usually used in molding compounds to provide freedom in adjusting physical, electrical and chemical properties, cost, changes in availability, etc., are included for reference. Some are fibrous in nature, and hence are sometimes referred to as reinforcing fillers. They may be used in loadings as high as 90 to 97%.[34]

a) *Cotton Flock*—from cotton scrap or linters.

b) *Wood Flour*—obtained by grinding soft fir, pine, etc., and some hardwoods such as maple.

c) *Shell Flour*—ground pecan, peanut or walnut shells.

d) *Alpha Cellulose*—obtained by alkaline treatment of wood pulp.

e) *Jute and Sisal*—coarse fibers of sisal and offal from regular cutting operations are used; jute, a fiber from an East Indian plant, is used as chaff or as woven burlap cloth.

f) *Chopped Paper*—strips and fragments cut from resin-impregnated paper.

g) *Lignin Fillers*[35]—the natural resin lignin is contained in Douglas fir bark fibers, cork flakes and fine powders may actually replace a portion of the synthetic resin in a molding compound formulation.

h) *Soybean Meal*

i) *Keratin*—feathers, hoofs and bristles, calcined prior to use as fillers.

COLORING AGENTS AND APPEARANCE IMPROVERS

Color Pigments

Coloring agents for polyesters, epoxies and the general class of low-pressure molding, addition-polymerizable thermosetting resins consist of inorganic and organic pigments and some dyes dispersed, at approximately 50% concentration, in a diallyl phthalate resin or other vehicle compatible with the particular molding material. The inorganic pigments have good stability against oxidation and exposure to ultraviolet light. The organic pigments provide superior brightness and color strength but their stability is not as permanent as that for the inorganic pigments.

Some pigments are simply mixed by stirring into the carrier vehicle, but best dispersion is accomplished using a three-roll paint mill, especially when pigments which tend to agglomerate are to be prepared. Incorporation of the pigment-plus-vehicle, or color concentrate into the resin to be used may be made by stirring. Quantities of concentrate naturally depend upon color to be used, but quantities vary from 0.5% by weight or less for translucency in resins for structural panels, to between 1 and 5% in matched-die molding and premix batches, to 10 or more per cent in gel coats. Tints may be produced by adding an amount of white pigment concentrate equal to the colored pigment concentrate used.

In many instances, it is more desirable economically and in terms of quality to apply a surface color coat than to color the entire body of the RP part. This of course is the reason for gel coating, and the practice is more easily adapted to hand-lay-up and manual molding procedures than heated die processes. Some liquid-gel coat applications to heated-dies for matched-die molding have been successful.[36] Other dry-resin processes are under development.

A variety of different effects may be achieved by masking and applying several different-colored gel coats, by incompletely mixing or stirring in batches of different-colored gel coats or molding resins to produce marbleized effects, and also by using transparent colorants in a fairly thick RP section to produce the illusion of depth.

It is virtually impossible in a limited space to provide a complete listing of the many inorganic and organic pigments available and accompany it with reliable data on the performance of that pigment in all types of RP molding methods and exposure conditions. Polyesters are more limited than epoxies for variety of pigments which may be used successfully. This is due to

the oxidative nature of the catalysts used with polyesters and also the sensitivity of the resins to ultraviolet exposure. Silicone resins are still more difficult to pigment than the polyesters, and phenolics are the most limited of the thermosets due to their innate dark color. Phenolics or their curing processes do not degrade as many coloring pigments as do polyester, however.

Titanium dioxide and antimony trioxide whites in paste-color concentrate form provide good performance with polyesters. Iron oxide and carbon blacks are used, the iron oxide being more stable. Carbon blacks or iron oxide blacks are, for the most part, the only coloring agents which may be used as dry pigments according to the accepted practice of formulating premix batches. Other coloring agents and their functions and reliability may be better assayed by consulting manufacturers' listings and the other references cited.[m, m, n] Table III-4.2 summarizes functions of the colorants in thermosetting resins.

Stability of pigments was measured in matched-die molding processes, and several conclusions drawn.[m] It was found that color hue or intensity was altered by amount and type of other filler used, changes in the weight of veil mat used, and by poor control over changes in the techniques used in mixing. No color changes resulted from minor adjustments in catalyst concentration nor from molding times or temperatures. Optimum concentration was determined to be 5% by weight.

Pearlescent pigments are used widely in the plastics industry, but to a fairly limited extent in RP. Polyester castings are substantially improved in appearance by addition of pearlescent pigments. Shirt and suit buttons and decorative plaques, etc., are examples. Pearlescent or nacreous (from "nacre," a small shellfish that yields mother of pearl) pigment may be supplied either dry or in a fluid vehicle, and the base pigment may be either natural, from fish scales, or synthetic, from lustrous inorganic crystalline substances[m] (basic lead carbonate).

The effects which result in pearlescence are strictly optical, and depend upon selective reflectance of light from the many small platelets in the pearlescent pigment. Approximately 12% by weight of pearlescent pigment is required. The platelets must be completely dispersed and oriented properly. The best orientation results when some motion or agitation is provided following addition of the pigment and prior to gelation.

Unfortunately, copresence in the resin matrix of glass-fiber reinforcement interferes with pearlescent dispersion and orientation, and results not in a pearly luster, but in a diffuse white color, not 100% opaque. Button castings would no doubt be improved if they were reinforced. They would also be made more economically if they could be sectionally cut from cast rods or cylinders, instead of being stamped from partially cured flat sheets which leave 20 to 25% waste. However, the cylinder method does not provide proper uniformity of dispersion and orientation, and is thus far impractical. Methods of molding buttons from dry, polymerizable powders have also been investigated without successful pearlescent effects.

Pigments are available which provide lustrous metallic and/or pearl-like finishes in thermoset plastic surfaces. These do not require the high concentrations of pearlescent pigments. They are just as readily dispersed, and are not as sensitive in arriving at the proper platelet orientation as are the pearlescents.

Finite-sized metal flake powders of aluminum, bronze and anodized (colored) aluminum may also be used.

Reflective glass spheres 0.020-inch diameter and less have been incorporated into a clear, light-stable polyester resin for use as centerline, side-of-the-road or overhead highway markers. It is necessary to incorporate the glass beads very close to the surface of the part, maintaining a very thin resin coating so as not to interfere with bead reflectance.

Light Stabilizers

Polyesters may be made fairly water-clear during manufacture, but epoxy resin manufacturers are never able to completely avoid an amber tint. Polyesters are subject to solarization, becoming more yellow or darker, and epoxies also darken from their original color upon weathering.

The polyesters are of major concern as regards weathering problems by virtue of their wide use in structural panels and molded housings intended for outdoor use.[n] Also, weight loss of general-purpose polyester resins exposed to outdoor weathering has been measured at 1% per year, thus accounting for blooming of fibers placed close to the surface during molding.

Precautionary measures taken to limit the discoloration on weathering have proved successful. Materials have been provided which absorbed ultraviolet light, thereby preventing or delaying oxidation of the resin. Triphenyl and dibutyl phosphites, phenyl salicilate, 2,4-dihydroxybenzophenone and derivatives have been successfully used, as well as many other proprietary compounds.

The problem of erosion of the resin may be overcome by creating a resin-rich surface, by applying a film during lay-up which becomes a portion of the finished laminate, or by permitting erosion to occur and rejuvenating the RP structure when necessary (every 3 to 5 years) by application of a lacquer based on one of the following compositions:[n]

For Fire-Retardant Panels:

	Per Cent by Weight
1. Lacquer base No. 100 (Hooker Electrochemical Co., Niagara Falls, N. Y.)	33.4
Methylethyl ketone	20.0
Xylene	6.6
Toluene	40.0
Total	100.0

For Standard Panels:

2. Polyester surface coating lacquer No. X 15 (Ram Chemicals, Gardena, California).
3. Acro 13-30A Acrylic lacquer (Nopko Paint and Varnish Works, Houston, Texas).

Translucent architectural panels are made usually with only token amounts of filler incorporated. Usually only 1% or less of a finely divided silica is incorporated to provide light diffusion. Larger amounts of any filler drastically and undesirably reduce light transmission. A problem exists also in the fact that unfilled panels have high transmission in the infrared portion of the spectrum, causing personal discomfort due to excessive heat transmitted through such paneling material when it is used as a patio roof covering or awning.

A partial solution to these problems has been at least approached by incorporation of a clay type filler with such fine particle size that a loading of 33% in corrugated structural paneling allows a high light transmittance of 62 to 65%. The high filler loading also beneficially reduces infrared transmission to provide a corresponding improvement in personal comfort.